

## Translation

(19) Patent Office of Japan (JP)

(12) **Gazette of Unexamined Patent Applications (A)**

(11) Unexamined Patent Application Disclosure

[Kokai] No.: **Heisei 3-275502**

(43) Disclosure Date: December 6, 1991

(51) Int. Cl.<sup>5</sup>  
C 01 B 6/21

Identification Symbol

Patent Office Ref. No.  
9041-4G

Request for Examination: not yet requested    Number of Claims: 1    (Total of 5 pages)

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(54) Title of the Invention: Method of Preparation of Sodium Borohydride

(21) Patent Application [Tokugan] No.: Heisei 2-75656

(22) Filing Date: March 27, 1990

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### **Scope of Patent Claims**

#### Claim 1

A method of preparation of sodium borohydride comprising the reaction of a trialkoxy boroxine expressed by the General Formula  $(R-O-B-O)_3$  with sodium aluminum hydride (in the formula, R represents an aliphatic, alicyclic, or aromatic hydrocarbon group).

#### Details of the Invention

##### Industrial Field of Application

The present invention relates to a method of preparation for sodium borohydride, a useful reducing agent.

## Prior Art

The present applicants previously applied for a patent on the manufacture of sodium borohydride ( $\text{NaBH}_4$ ) by reacting a trialkoxy boran expressed by  $\text{B(OR)}_3$  with sodium aluminum hydride ( $\text{NaAlH}_4$ ) (see Japanese Application Heisei 1-28584). This reaction takes place according to the below listed reaction formula (3):



This method embraces a number of advantages.

For example, the reaction can be implemented under moderate temperature conditions, and unlike methods of the prior art, after the reaction, the  $\text{NaBH}_4$  can be recovered in a highly pure form without performing complex extraction procedures.

## Problems To Be Resolved by this Invention

However, the B content in trialkoxy boran is low, and as a result, in order to produce large quantities of  $\text{NaBH}_4$ , a very large volume of the trialkoxy boran must be used as the boron source. Accordingly, there are limits to the amounts of  $\text{NaBH}_4$  that may be prepared in the same reaction vessel.

## Means Used To Resolve Problems

The present inventors performed exhaustive research to resolve the foregoing problem and that effort resulted in the completion of the present invention.

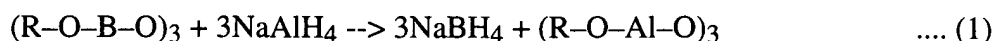
To wit, this invention presents a method of preparation of sodium borohydride comprising the reaction of a trialkoxy boroxine expressed by the General Formula  $(\text{R-O-B-O})_3$  with sodium aluminum hydride (in the formula, R represents an aliphatic, alicyclic, or aromatic hydrocarbon group).

The use of trialkoxy boroxine as a source of B to prepare  $\text{NaBH}_4$  is completely unknown to the prior art.

The use of trialkoxy boroxine has the advantage that it contains about twice the B content of trialkoxy boran.

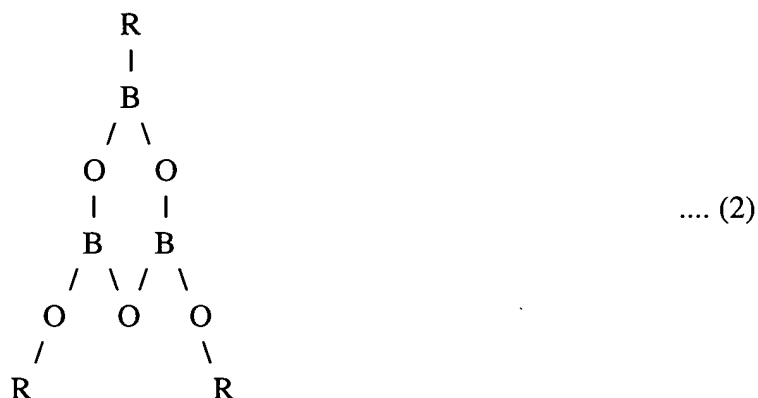
By its use of trialkoxy boroxine as the B source, the method of this invention allows the manufacture of a novel  $\text{NaBH}_4$  not known to the prior art.

The invention will be explained in detail below. The reaction of the invention takes place according to the below listed reaction formula (1).



To wit, trialkoxy boroxine is reacted with sodium aluminum hydride to produce sodium borohydride and a byproduct of an alkoxy aluminum compound.

First, the trialkoxy boroxine used in this invention may be synthesized by conventional methods such as by the dehydration reaction of alcohol with boric acid as described in Japanese Patent Showa 41-6751. It is a cyclic compound such as shown in the below listed formula (2).



Specific examples of trialkoxy boroxines include: trimethoxy boroxine  $[(\text{CH}_3\text{-O-B-O-})_3]$ , triethoxy boroxine  $[(\text{C}_2\text{H}_5\text{-O-B-O-})_3]$ , tripropoxy boroxine  $[(\text{C}_3\text{H}_7\text{-O-B-O-})_3]$ , tributoxy boroxine  $[(\text{C}_4\text{H}_9\text{-O-B-O-})_3]$ , etc.

Further, the presence of small amounts of trialkoxy boran, a byproduct resulting from variations in the ratio of boron to alcohol during the synthesis of boroxine, presents no problems to the production of  $\text{NaBH}_4$ . Thus, the use of trialkoxy boroxine has a number of attendant advantages.

Compared to the conventional source of B used in the prior art, trialkoxy boran, the use of trialkoxy boroxine used in this invention has a much higher B content—about twice as much for the same weight.

For example, tri-n-butoxy boroxine has 2.3 times more boron than tri-n-butoxy boran.

The volume of B per gram-atom in tri-n-butoxy boroxine is 43%.

As a result, for example, if a THF solution of  $\text{NaAlH}_4$  is reacted with it to produce  $\text{NaBH}_4$ , when the trialkoxy boroxine of this invention is used as the source for boron, it is possible to manufacture 1.1 to 1.3 times more  $\text{NaBH}_4$  than if an equivalent amount of the conventional trialkoxy boran were used.

Further, as was described above, both trialkoxy boroxine and trialkoxy boran are synthesized by a dehydration reaction of alcohol with boric acid, but the amount of alcohol used per each B atom when synthesizing trialkoxy boroxine is only 1/3 of that required to synthesize trialkoxy boran. This makes it possible to shorten the time required for the dehydration reaction.

As a result, trialkoxy boroxine is a less expensive source of boron than trialkoxy boran.

Further, after the reaction, when trialkoxy boroxine is used instead of trialkoxy boran, less of the byproduct of alkoxy aluminum compound is generated.

This simplifies the filtering or the extraction operation used to yield the  $\text{NaBH}_4$ .

This process further reduces operating costs because alcohol can be recovered from the alkoxy aluminum compound generated as a byproduct and refined for reuse. The cost of the process has been reduced because the amount of alcohol that needs to be handled has been reduced to 1/3.

Further, the  $\text{NaBH}_4$  synthesized from trialkoxy boroxine exhibits a larger particle size, with few fine particles generated. This helps to prevent lumping of the resulting powder and makes it easier to handle.

Thus, when such  $\text{NaBH}_4$  powder is dumped into a hopper or the like, no bridging or other problems occur, and it is easy to package in and remove from bags.

There are no particular restrictions upon the method used to prepare the  $\text{NaAlH}_4$  that is used to synthesize the  $\text{NaBH}_4$ ; methods known to the art may be used. For example, synthesis can be performed with metallic sodium, metallic aluminum powder and hydrogen (see Japanese Patent Application [Kokai] Disclosure Showa 58-213601). However, it is desirable to remove any reaction residues of metallic powder in order to synthesize a highly pure  $\text{NaBH}_4$ .

Next, the reaction of Formula (1) of this invention is performed in the presence of a solvent.

It is preferable that the solvent used in the reaction be able to dissolve both, or at least one of the alkoxy boroxine and the  $\text{NaAlH}_4$ . Due to the limited solubility of  $\text{NaAlH}_4$  in general, it is preferable to use an ether in which it is soluble. Also, it is preferable to mix in a small amount of aliphatic or aromatic hydrocarbon solvent to better control the reaction.

Further, consideration should be given to whether or not the solvent used will dissolve the byproduct alkoxy aluminum compound or not, since this impacts upon whether the isolation of the  $\text{NaBH}_4$  can be performed by simple filtration, or whether more complex extraction methods will be required. Solvents which will dissolve the alkoxy aluminum compounds include tetrahydrofuran (THF), and mixtures of THF and aliphatic or aromatic hydrocarbon solvents.

The intermediate of  $\text{NaAlH}_4$  reacts with water and  $\text{NaAlH}_4$  and  $\text{NaBH}_4$  can decompose to generate  $\text{H}_2$  so there is a risk of explosion if  $\text{O}_2$  is present. Accordingly, the reaction must be implemented in an environment free of water and oxygen.

(1) If the reaction temperature is too low, the reaction will not proceed, but high reaction temperatures are not required. Generally, a reaction temperature in a range of 50 to 100°C is preferable, and the reaction will proceed satisfactorily at the boiling point of THF.

This reaction is exothermic. Generally, the reaction is best implemented in a gentle but sustained reflux of THF. When the dropwise addition is completed and reflux is halted, it is preferable to maintain the temperature until the reaction is completed.

The trialkoxy boroxine may be added to the solution of the  $\text{NaAlH}_4$  or vice-versa.

Each mole of trialkoxy boroxine contains 3 gram-atoms of boron.

Accordingly, with regard to the mixture ratios, the ratio of the boron to the gram-atoms of Al contained in  $\text{NaAlH}_4$  (B/Al) should generally range from 0.8 to 1.5, preferably, from an economic perspective, 1.0 to 1.2.

In cases where the reaction solvent is one in which the byproduct of alkoxy aluminum compound is insoluble, after the reaction, one must use extraction or another method to separate the  $\text{NaBH}_4$  from the alkoxy aluminum compound. Examples include extraction with liquid ammonia, extraction with an amine, or extraction with an aqueous alkali solution.

Naturally, if the byproduct alkoxy aluminum compound is soluble in the reaction solvent, then the isolation of the  $\text{NaBH}_4$  powder can be accomplished easily by filtration. A normal filtration apparatus is adequate for this filtration process.

After filtration, the product is solvent-washed and dried to yield highly pure  $\text{NaBH}_4$ .

Since the byproduct alkoxy aluminum product can be decomposed by hydrolysis, it is possible to recover the alcohol and recycle it, but it may also be used as a chemical or pharmaceutical raw material, such as for the manufacture of alumina.

### Examples

Examples will be presented below to explain the present invention in further detail.

#### Example 1

A 1-liter 4-necked flask equipped with a stirrer, burette and reflux condenser was purged with nitrogen. Then, 54 g (1.0 mole) of  $\text{NaAlH}_4$  dissolved in 362 g of tetrahydrofuran was added to the flask.

With the burette, 105 g (0.35 mole) of tri-n-butoxy boroxine was added to the flask dropwise over a 4-hour period. The B/Al ratio was 1.06. The solution temperature was maintained at the boiling point of tetrahydrofuran, and the reaction was continued at that temperature for an hour after completion of the addition.

The product was isolated by filtration with a G-4 glass filter, and then it was washed in 400 g of tetrahydrofuran, filtered, and dried under reduced pressure at  $100^\circ\text{C}$ .

34 g (0.9 mole) of white crystalline  $\text{NaBH}_4$  was obtained at a 90% yield. Iodometry revealed the purity to be 99.1%. Also, the average particle diameter of the  $\text{NaBH}_4$  powder was 20 to 30  $\mu$ . The byproduct alkoxyamine compound was decomposed to recover 77.9 g (1.05 mole) of n-butanol.

#### Example 2

The method of Example 1 was followed except that instead of using tri-n-butoxy boroxine, 86 g (0.40 mole) of tri-n-ethoxy boroxine was used. The B/Al ratio was 1.2.

This produced 33 g (0.88 mole) of  $\text{NaBH}_4$  white crystals at a yield of 88%.

Iodometry revealed a purity of 99.0%. The average particle diameter of the  $\text{NaBH}_4$  powder was 20 to 30  $\mu$ .

#### Comparative Example 1

The method of Example 1 was followed except that 241 g (1.05 mole) of tri-n-butoxy boran was substituted for the tri-n-butoxy boroxine.

The gram-atoms of B in the tri-n-butoxy boran were equivalent to the amount contained in the tri-n-butoxy boroxine used in Example 1.

This produced 36 g (0.94 mole) of  $\text{NaBH}_4$  white crystals at a yield of 94%.

The average particle diameter of the  $\text{NaBH}_4$  powder was about 10  $\mu$ .

The total amount of the reaction components charged into the 4-necked flask was 657 g, as compared with the 521 g total of Example 1. It thus required the use of 1.28 times more reagent, 1.21 times more when corrected for the experimental yield. Thus, it took a larger amount of raw materials to prepare the same amount of  $\text{NaBH}_4$ , thereby exhibiting lower productivity.

The byproduct butoxy aluminum was decomposed to recover 233.4 g (3.15 mole) of n-butanol. Thus, performing this recovery operation was more of a requirement than it was for Example 1 since the amount of n-butanol recovered was 3-fold higher.

#### Effects of the Invention

One can appreciate all of the benefits of the present invention's method of preparation of  $\text{NaBH}_4$  compared with our previous proposal for using  $\text{NaAlH}_4$  (Japanese Application Heisei 1-28584).

Further, by using this novel source of boron, it is possible to further reduce production costs and improve productivity. Also, the larger particles of the resulting  $\text{NaBH}_4$  powder make it easier to handle.

Further, the need to perform cumbersome extraction operations may be completely obviated by selecting a solvent that will dissolve the alkoxy aluminum compound. It is thereby possible to obtain highly pure  $\text{NaBH}_4$  by means of a simple filtration operation.

Due to the many reasons detailed above, using the trialkoxy boroxine as the source of boron in the method of this invention provides significant benefits to the industry.